Not for Publication
Presented Before the Division of Gas and Fuel Chemistry
American Chemical Society
Boston, Massachusetts, Meeting, April 5-10, 1959

GAS-LIQUID CHROMATOGRAPHIC ANALYSIS OF AROMATIC HYDROCARBONS BOILING UP TO 218°C. IN A LOW-TEMPERATURE COAL TAR

Ta-Chuang Lo Chang and Clarence Karr, Jr.
Low-Temperature Tar Laboratory
Bureau of Mines
U. S. Department of the Interior
Morgantown, W. Va.

INTRODUCTION

Detailed analysis of low-temperature coal tar will lead to a clearer understanding of the chemical structure of the tar and thus help both in the study of the mechanism of carbonization and the development of uses for the tar.

As a part of a broad low-temperature coal tar characterization program, this paper presents the results of analysis of the aromatic hydrocarbons, boiling up to 218°C., which are present in the neutral oil portion of a low-temperature bituminous coal tar.

Previously only 28 aromatic hydrocarbons boiling between 80 - 218°C. were found in low-temperature bituminous coal tars by means of older analytical techniques[1,2,3,4]. In 1956 Grant and Vaughan[5] described the gas-liquid chromatographic analysis of aromatic hydrocarbons in coal tar naphthas, and identified benzofuran, an unspecified methyl styrene and six other aromatic hydrocarbons boiling up to 178°C. in two low-temperature coal tars; of these, only the methyl styrene was not previously reported.

In the present work, gas-liquid chromatography, together with other modern techniques, was used for analysis, and 52 aromatic hydrocarbons boiling up to 218°C. were found in a low-temperature bituminous coal tar, and their quantities determined.

A correlation was established between relative retention and boiling points for some alkyl benzenes, whereby the identification of several other aromatic hydrocarbons was made possible.

Besides indans, benzofurans, and indenes, the aromatic hydrocarbons identified are methylated, ethylated, or propylated benzenes. Up to the present time, no butyl benzenes have been found in this particular tar.

Of the 52 compounds found, 27 had not been previously reported to be present in a low-temperature bituminous coal tar.

Another phase of the work concerning the analysis of higher boiling aromatic hydrocarbons such as biphenyls and alkyl naphthalenes, of which several have already been identified in this laboratory, is being completed and the results will be reported at a later date.

EXPERIMENTAL WORK AND RESULTS

I. Preparation of Aromatic Hydrocarbon Concentrates from the Coal Tar for Gas-Liquid Chromatography

Isolation of neutral oil from tar distillate

The tar used in this work was made from a West Virginia, Pittsburgh-seam, high-volatile bituminous coal in a fluidized carbonization pilot plant at about 480-510°C. The raw tar was de-ashed, dehydrated, and topped to about 175°C. at the plant. The tar distillate had been obtained in this laboratory under very mild temperature conditions calculated to be equivalent to about 350-360°C. at atmospheric pressure with a yield of 20.8 weight percent of the tar in the main distillate and less than 1 percent collected in a dry ice trap.

About three liters (2660 g.) of the main distillate were extracted according to the method of Fisher and Eisner[6] to remove tar acids and tar bases. The neutral oil thus obtained was washed three times with an equal volume of water. After passing it through a filter made of three layers of filter paper on a funnel, the oil was dried in a desiccator over anhydrous calcium chloride for a week. About 2400 ml. (2180 g.) of dry neutral oil, corresponding to 82% by weight of the distillate and 16.9% by weight of the tar, was obtained.

Fractional distillation of the neutral oil

A 698 g. charge of the neutral oil was fractionally distilled in a Podbielniak Hyper-Cal high-temperature automatic distillation apparatus. The column was 8 mm. by 36 inches and was packed with Heli-Grid Packing. The end point chosen for this distillation was a pot temperature of 200°C. to avoid any significant thermal alterations. The results of this distillation are given in Table I. Equivalent atmospheric boiling points were estimated from a standard nomograph.

Separation of the neutral oil fractions into chemical types by displacement chromatography

The silica gel adsorption method based on displacement chromatographic techniques which have been applied to petroleum distillates[7] and shale-oil naphthas[8] was adapted for separating the aromatic hydrocarbons from saturates and unsaturates.

The column chosen for this work consisted of an upper section 22 cm. long and 10 mm. I.D. and a lower section 138 cm. long and 3 mm. I.D. The entire column was jacketed to provide water for cooling or heating as required.

The column was packed with Davison Grade 950 silica gel, 60-200 mesh, which had been freshly activated at 160°C. for four hours just before packing. About 26 g. of silica gel were needed for the column. A fresh batch of silica gel was used for each run.

The sample was charged to the column, using about 3 p.s.i.g. oxygen-free nitrogen pressure. The desorbents selected were two different alcohols, the choice being made on the basis of the relative kinematic viscosities of the sample and the alcohol. An alcohol could be selected for each fraction so that its viscosity would be somewhat greater than that of the fraction. The alcohols were also chosen for desorbents on the basis of miscibility with the samples, and ease of removal from the last portions of the charge desorbed. After the sample was charged to the column, it was followed immediately by the desorbent with about 10 p.s.i.g. nitrogen pressure.

TABLE I

FRACTIONATION OF NEUTRAL OILS IN PODBIELNIAK STILL

Charge: 16.92 wt. % of the tar
698 g.
Distillate: 360 g. = 51.6%
Residue: 338 g. = 48.4%

Fraction no.	Head temp., °C., 50 mm.	Estimated b.p. °C., 760 mm.	Weight, g.
1	77.5 - 87.5	163 - 180	4.43
2	87.5 - 94.0		
3	94.0 - 101.4	180 - 190	3.94
4	101.4 - 104.3	190 - 192	4.53
5	104.3 - 109.0	192 - 198	9.81
6	109.0 - 114.5	198 - 202	9.61
7	114.5 - 118.3	202 - 210	25.95
8	118.3 - 121.8		
9	121.8 - 124.2	210 - 213	5.29
10	124.2 - 126.5	213 - 220	17.88
11	126.5 - 130.9		
12	130.9 - 132.9	220 - 225	14.80
13	132.9 - 134.2		
14	134.2 - 137.3	225 - 230	12.78
15	137.3 - 139.9	230 - 233	18.36
16	139.9 - 141.5	233 - 235	17.11
17	141.5 - 141.9	235 - 236	14.13
18	141.9 - 145.9	236 - 240	11.54
19	145.9 - 149.4	240 - 243	18.46
20	149.4 - 151.6	243 - 246	18.84
21	151.6 - 153.5	246 - 248	19.22
22	153.5 - 155.0	248 - 250	20.57
23	155.0	250	18.55
24	155.0 - 155.8	250 - 251	6.34
25	155.8 - 157.8	251 - 253	18.46
26	157.8 - 158.0	253 - 253	18.46
27	158.0 - 159.9	253 - 254	18.07
28	159.9 - 162.0	254 - 256	21.34
29	162.0 - 163.0	256 - 260	11.53
		Total	360.00

The operating temperature chosen for each sample depended on the melting points of the expected components in the fraction. If some of them were crystalline at room temperature, a temperature near the melting points of the components was used.

Fractions were obtained with an automatic fraction collector which counted drops photoelectrically and maintained the fractions in an atmosphere of oxygen-free nitrogen.

Usually only the very last fraction was contaminated by the desorbent. The desorbent was removed by extracting with 80 to 90% glycerine, and the glycerine was then removed with several water washings. The alcohol- and glycerine-free sample was dried overnight over anhydrous calcium chloride in a partially evacuated desiccator. The refractive index was obtained on each fraction, and by comparing these values with literature values for pure hydrocarbons in the boiling range of the charge, it was readily estimated where the paraffins and naphthenes, olefins, aromatics, and neutral oxygen, nitrogen and sulfur compounds were located among the fractions. With this technique, no sharp border lines could be expected between two adjacent types. However, it was found that overlapping occurred only in the very first and the very last fractions of any one type.

Since this paper covers the first six distillate fractions, boiling from 163° - 202°C., the data on displacement chromatography for only these fractions are given in Table II. About 17 drops per displacement fraction were collected, except for the last one, which consisted of about 50 drops.

II. Analysis of Aromatic Hydrocarbons by Gas-Liquid Chromatography

Apparatus and operating conditions

A Perkin-Elmer Model 154C Vapor Fractometer was used. The response range of the recorder was 0-11 millivolts and the speed of the chart was 3.75 in./hr. The peak areas produced by components of the sample on the chromatogram were measured with a planimeter.

The column for this work was made from a 15 ft. x $\frac{1}{4}$ in. O.D. copper tubing filled with approximately 50 g. of packing made of 25% Apiezon L grease on 30-60 mesh fire brick. After packing, the column was coiled to fit into the column chamber of the Fractometer.

The temperature chosen for the analysis was 150°C., approximately 10°C. below the lowest boiling fraction and 50°C. below the highest boiling fraction. Samples were injected with 10 or 50 microliter syringes. The carrier gas was helium, admitted to the column at a pressure of 12 lb./in.^{2}, corresponding to a flow rate of 95 ml./min. The outlet pressure was atmospheric. The voltage for the bridge of the thermoconductivity detector was 8 volts and the most sensitive range was used. Throughout the work, the temperature stayed within $\pm$ 0.1°C. and the carrier gas pressure and the voltage of the bridge stayed constant.

The efficiency of the column under these conditions, referring to n-propylbenzene and to 1,2,3,5-tetramethylbenzene, was 3520 and 3885 theoretical plates, respectively, calculated by using the equation[9], No. of theoretical plates = $16(x/y)^2$, where y = length of peak base line (as defined), and x = length from start of run to middle of base line section.

TABLE II

DISPLACEMENT CHROMATOGRAPHIC SEPARATION OF NEUTRAL OIL DISTILLATE FRACTIONS INTO CHEMICAL TYPES

Distillate fraction no.	1 + 2	3	4	5	6
Weight of charge, g.	1.77	3.15	3.60	7.40	7.70
Desorbent	Isopropyl alcohol	Isopropyl alcohol	Isopropyl alcohol	Isopropyl alcohol	Butyl alcohol
Saturates + some olefins					
Number of fractions	5	3	4	7	5
Refractive index range, n_D^{20}	1.3930-1.3941	1.4381-1.4832	1.4252-1.4471	1.4328-1.4695	1.4400-1.4683
Total weight, g.	0.74	0.61	1.20	2.11	1.93
Aromatics + some olefins + some O,S compounds					
Number of fractions	4	5	5	9	12
Refractive index range, n_D^{20}	1.3941-1.5007	1.4832-1.5310	1.4911-1.5397	1.4912-1.5545	1.4895-1.5601
Total weight, g.	0.70	2.29	2.17	4.32	5.21
N, S, and O compounds retained on column	0.33 g.	0.25 g.	0.23 g.	0.97 g.	0.56 g.
Weight of aromatic hydrocarbons identified by GLC	0.57 g.	1.95 g.	1.66 g.	4.30 g.	4.81 g.

Sample collecting system for gas-liquid chromatography

The original fraction collecting system for the Perkin-Elmer instrument has a short length of 1/8 in. stainless-steel tubing leading from the detector cell to an external syringe needle adaptor that has a 3-way syringe valve. This is intended for attaching a short needle which can be inserted through a rubber serum bottle cap at the bottom of a solvent-filled tube for washing effluent gas in order to collect fractions. However, this type of collector was found to be unsatisfactory in most cases.

A new fraction collecting system was devised, which would take advantage of the existing needle adaptor. This involved heating the stainless-steel tubing electrically to prevent the fractions from condensing, and using 6 inch—18 gauge syringe needles cooled with powdered dry ice as fraction collectors. Holders for dry ice powder were made from 110 mm. lengths of 18 mm. O.D. glass tubing, which were wrapped with aluminum foil and asbestos string, and plugged at one end with 12 mm. thick cork stoppers, each having a small hole in the center for entry of the needles. To collect the material producing a chromatogram peak, one of the needles was fastened to the upright needle adapter and one of the dry ice jackets was slipped down over the needle, the insulating cork plug resting on the hot needle hub. The jacket was carefully packed with dry ice powder and the 3-way valve turned to admit effluent gas to the needle. After collecting a sample, the needle was removed, a Teflon plug inserted at the hub end and a little polyethylene tube slipped over the needle end, and placed in a dewar flask containing dry ice. The infrared spectrum of the sample was subsequently obtained in a 0.05 mm. or 0.1 mm. microcell for identification of the components. The infrared microcell was filled by inserting the needle tip into the cell and introducing a fraction of a drop of carbon disulfide into the needle hub. However, in some instances, it was necessary to wash out the needle with about $\frac{1}{2}$ ml. carbon disulfide, collecting the solution in a 1-ml. beaker and carefully evaporating off solvent with a gentle stream of nitrogen until about one drop of solution remained. This was then placed into the microcell by capillary action, using the capillary tubing of the cell. Good infrared spectra were obtained with about 1-mg. hydrocarbon, and, in particular, there was no contamination from compounds producing adjacent peaks.

General approach for identification

The retention times of 42 aromatic hydrocarbons boiling in the range of the neutral oil samples were obtained, for the purpose of preliminary identification of the unknowns. The relative retentions at 150°C. and 200°C. of the 42 aromatics, referred to n-propylbenzene, are shown in Table III. These relative retention values can be considered to be either relative retention times or relative retention volumes.

The aromatic fractions obtained by displacement chromatography of the first six distillate fractions were individually examined by gas-liquid chromatography under the same conditions for the known compounds. To confirm the identification, the material producing each peak was collected for infrared spectrophotometric analysis. Three methods were used to identify the aromatic hydrocarbons present in the fractions.

The first method of identification consisted of a combination of conventional gas-liquid chromatography and infrared spectrophotometry. The retention times of unknown peaks were compared with those of known compounds for a preliminary identification. The material producing each peak was then collected in a microcell for an infrared spectrum, as previously described. The confirmation of identity was then made by comparing this spectrum with that of the known compound.

TABLE III

LITERATURE BOILING POINTS, RELATIVE RETENTIONS AND CALIBRATION FACTORS (f_C) OF SOME AROMATIC HYDROCARBONS

Compound	Literature b.p. °C., 760 mm.[a]	Relative[b] retention (150°C.)	f_C (150°C.)[c]	Relative[b] retention (200°C.)
Methylbenzene	110.626	0.36	1.02	0.48
Ethylbenzene	136.186	0.62	0.95	0.64
1,4-Dimethylbenzene	138.351	0.67	0.98	0.70
1,3-Dimethylbenzene	139.104	0.68	1.00	0.71
1,2-Dimethylbenzene	144.411	0.77	1.01	0.82
Isopropylbenzene	152.392	0.83	1.02	0.86
n-Propylbenzene	159.217	1.00	1.00	1.00
1-Methyl-3-ethylbenzene	161.305	1.06	1.01	—
1-Methyl-4-ethylbenzene	161.989	1.09	1.08	1.06
1-Methyl-2-ethylbenzene	165.153	1.21	1.06	1.17
1,3,5-Trimethylbenzene	164.716	1.19	1.08	1.13
1,2,4-Trimethylbenzene	169.351	1.38	1.03	1.29
1,2,3-Trimethylbenzene	176.084	1.67	1.04	1.52
Indan	177.82	1.82	1.65	1.69
Isobutylbenzene	172.759	1.33	1.07	1.26
sec-Butylbenzene	173.305	1.34	1.08	1.27
n-Butylbenzene	183.27	1.77	1.04	1.56
1-Methyl-3-isopropylbenzene	175.14	1.39	1.07	1.27
1-Methyl-4-isopropylbenzene	177.10	1.48	1.04	1.35
1-Methyl-2-isopropylbenzene	178.15	1.58	0.94	1.42
1-Methyl-3-n-propylbenzene	181.80	1.71	1.03	1.51
1-Methyl-4-n-propylbenzene	183.30	1.76	1.03	1.58
1-Methyl-2-n-propylbenzene	184.80	1.90	1.07	1.67
1,3-Diethylbenzene	181.102	1.62	1.00	1.45
1,2-Diethylbenzene	183.423	1.81	1.06	1.60
1,4-Diethylbenzene	183.752	1.79	1.03	1.58
1,3-Dimethyl-5-ethylbenzene	183.75	1.82	1.09	1.59
1,2,4,5-Tetramethylbenzene	196.80	2.77	0.93	2.28
1,2,3,5-Tetramethylbenzene	198.00	2.87	1.06	2.33
Indene	182.44	1.92	1.10	1.80

(Table III Continued)

Compound	Literature b.p. °C., 760 mm.[a]	Relative retention (150°C.)[b]	f_C (150°C.)[c]	Relative retention (200°C.)[b]
1-Methylindene	199	2.22	1.20	1.98
2-Methylindene	208	3.48	1.15	2.96
1-Methyl-3,5-diethylbenzene	200.70	2.68	1.11	2.14
1,2,3,4-Tetrahydronaphthalene	207.57	3.84	2.05	3.13
1,4-Diisopropylbenzene	208.9	3.26	—	2.49
1,2-Diisopropylbenzene	209	3.06	—	2.51
Benzofuran	171.38	1.35	1.15	1.33
Naphthalene	217.96	4.68	1.14	3.51
1,3,5-Triethylbenzene	216.2	3.87	—	1.13
Pentamethylbenzene	231.8	7.08	—	4.87
β-Methylstyrene (trans)	178.26	1.64	1.09	1.47
α-Methylstyrene	165.5	1.22	1.11	1.14
1,4-Dimethyl-2-ethylbenzene	186.91	2.04[d]	—	1.73[d]
1,2-Dimethyl-4-ethylbenzene	189.75	2.17[d]	—	1.89[d]
1-Methylindan	190.6	2.30[d]	—	1.99[d]
1,2-Dimethyl-3-ethylbenzene	193.91	2.50[d]	—	2.06[d]
5-Methylindan	202.0	3.25[d]	—	2.67[d]
1-Methyl-3,4-diethylbenzene	203.6	3.00[d]	—	—
4-Methylindan	205.5	3.46[d]	—	2.81[d]
1,2,3,4-Tetramethylbenzene	205.04	3.48[d]	—	2.81[d]
3-Methylindene	205	3.50[d]	—	2.82[d]

[a] All values, except for benzofuran, from API Research Project 44, "Selected Values of Properties of Hydrocarbons and Related Compounds," Carnegie Institute of Technology, Pittsburgh, Pa. Benzofuran b.p. from J. N. Breston and A. W. Gauger, Proc. Am. Gas Assoc., 28 (1946) 492.

[b] Dead volume corrected.

[c] Defined in eq. 1.

[d] The relative retentions of these compounds were determined from tar components identified by I.R.

Retention times could not, of course, be obtained for those compounds for which authentic specimens were not available. A second method of identification was used for these compounds which involved the correlation curves of relative retentions and boiling points shown in Fig. 2 and explained in detail in a later section. Boiling points of the unknowns producing peaks were obtained from their relative retentions by these correlation curves, and were used as a preliminary means of identification. Since literature infrared spectra of a number of compounds were available, confirmation could be made in these instances.

For a third group of compounds, neither the retention times nor the infrared spectra of authentic specimens were available. However, from the correlation curves and the relative retentions of the unknown peaks, tentative identification could be made through the boiling points. Also by correlating infrared absorption bands and molecular structures, these tentative identities could be further substantiated.

To illustrate the first and second methods of identification, the chromatogram of a typical fraction is shown in Fig. 1, and the boiling points of the components producing the peaks, as obtained from the correlation curves, are presented in Table IV. Excellent agreement is shown between literature and predicted boiling points. The peak numbers in Fig. 1 are explained in Table IV. This chromatogram was produced by a 10μl. sample of an aromatic cut of $n_D^{20} = 1.5074$, from distillate fraction no. 5 in a boiling range of 192-198°C.

TABLE IV

IDENTIFICATION OF COMPONENTS PRODUCING ELUTION PEAKS IN THE GLC OF AN AROMATIC CUT FROM DISTILLATE FRACTION NO. 5

Peak no.	Relative retention	Compound identified	Relative retention of known compound	Boiling point, °C. Literature	Boiling point, °C. From correlation curve
1	1	n-Propylbenzene (added standard)	1	159.2	159.2
2	1.69	1-Methyl-3-n-propylbenzene	1.71	181.8	181.3
3	1.82	1,3-Dimethyl-5-ethylbenzene	1.82	183.8	183.5
4	1.89	1-Methyl-2-n-propylbenzene	1.90	184.8	184.8
5	2.02	1,4-Dimethyl-2-ethylbenzene	*	186.9	186.9
6	2.16	1,2-Dimethyl-4-ethylbenzene	*	189.8	189.1
7	2.29	1-Methylindan	*	190.6	191.0
8	2.46	1,2-Dimethyl-3-ethylbenzene	*	193.9	193.5
9	2.65	1-Methyl-3,5-diethylbenzene	2.68	200.7	200.7
10	2.79	1,2,4,5-Tetramethylbenzene	2.77	196.8	197.3
11	2.86	1,2,3,5-Tetramethylbenzene	2.87	198.0	198.2
12	3.00	1-Methyl-3,4-diethylbenzene	*	203.6	204.2
13	3.25	5-Methylindan	*	202.0	202.3
14	3.45	4-Methylindan	*	205.5	204.3

* Authentic specimens not available for determination of retention times.

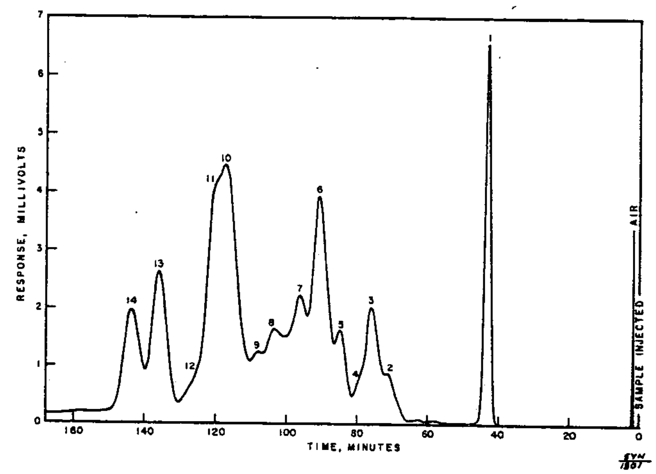

Fig. 1. Chromatogram of an aromatic cut obtained from distillate fraction no. 5.

Peak 1 is produced by n-propylbenzene, the internal standard, added to the cut for quantitative estimation of the components. The components producing peaks 2, 3, 4, 9, 10 and 11 were identified by comparing the retention times with those of known compounds. The components producing peaks 5, 6, 7, 8, 12, 13 and 14 were identified through their boiling points, obtained from their relative retention and the correlation curves. To confirm the identities, a 25 μl.-sample was used to produce enough material for each major peak for infrared spectrophotometric analysis. However, the minor ones, such as 4, 8, 9 and 12, were better confirmed by the infrared spectra of the material producing the corresponding peaks in the chromatogram of an adjacent aromatic cut.

Table V illustrates the third method of identification. It is to be noted that the identities of three compounds were further substantiated by considering the infrared absorption bands and probable molecular structures according to the correlations of Bellamy[10]. Two compounds were present in the last two distillate fractions (no. 5 and no. 6) in such small quantities that no satisfactory infrared spectra were obtained. Infrared spectra were obtained, however, for the components producing all the significant chromatogram peaks. It was observed that only a few weak absorption bands were unaccounted for by the compounds identified. The relative intensities of these bands were such that these unknown components could have been present in only trace amounts.

<u>Quantitative estimation of aromatic hydrocarbons</u>

The internal standard method was adapted for quantitative analysis of the samples, n-propylbenzene being selected as the standard. Keulemans, Kwantes and Rijnders[11] have demonstrated the use of an average calibration factor, f_C, defined as follows, for calibrating areas and percentages for a component, and an internal standard for obtaining precise quantitative analysis of light hydrocarbons:

$$f_C = A_s W_c / A_c W_s \qquad (1)$$

where A_s and A_c are the areas for the internal standard and component in the mixture, and W_c and W_s are the weight percentages of the component and the standard.

In order to investigate the deviation of the average calibration factors of aromatic hydrocarbons from the actual values in a certain range of concentrations, eight pure compounds, namely, 1-methyl-3-ethylbenzene, 1,3,5-trimethylbenzene, indan, 1,3-diethylbenzene, indene, 1,3-dimethyl-5-ethylbenzene, 1,2,3,5-tetramethylbenzene, and 1,2,3,4-tetrahydronaphthalene, were used. Three solutions of each compound in different concentrations, about 15%, 30%, and 60% by weight, were prepared in n-propylbenzene. Using these 24 solutions, the f_C values were then calculated from the weight percentages and the peak areas produced by the components in their chromatograms. It was found that the average f_C in the concentration range of 15-60% by weight had a maximum deviation of only about $\pm$ 3% from the actual values, and the best results were obtained at concentration ranges of 30-60%. This is considered accurate enough for estimating the amounts of aromatic components present in such a complex mixture as coal tar. The f_C values for the rest of the aromatic hydrocarbons were determined only once at 150°C. at a concentration of 40-50%. These f_C values are shown in Table III and were used to determine the weight percentages of all aromatic hydrocarbons in the fractions. For those compounds which were not available in this laboratory but found to be present in the sample, the f_C value of its isomers or of a structurally similar compound was used.

Two synthetic blends were analyzed by using these f_C values and the results are shown in Table VI.

TABLE V

DATA FOR TENTATIVE IDENTIFICATION OF FIVE ALKYLBENZENES

Name of compound	Literature b.p., °C., 760 mm.	Relative retention of the unknown peak	B.p., °C., obtained from the correlation curve	Infrared spectral-structural correlations
1,4-Dimethyl-2-isopropylbenzene	196.2	2.38	196.8	—
1,3-Dimethyl-2-n-propylbenzene	207.6	3.35	207.8	—
1,4-Dimethyl-2-n-propylbenzene	203.6	3.04	203	12.23 μ(S): 2H out-of-plane deformation vibration 11.39 μ(M): 1H out-of-plane deformation vibration 9.12 μ(W); 9.47 μ(W); 9.90 μ(MW) suggest 1,2,4-substitution of benzene ring Probable structure: 1,2,4-trialkylbenzene
1-Methyl-2,4-diethylbenzene	205.0	3.10	205.3	12.40 μ(S): 2H out-of-plane deformation vibration 11.30 μ(M): 1H out-of-plane deformation vibration 9.60 μ(W); 9.70 μ(W); and 8.65 μ(W) suggest 1,2,4-substitution of benzene ring Probable structure: 1,2,4-trialkylbenzene
1,2-Dimethyl-3-n-propylbenzene	210.7	3.64	210.5	12.81 μ(S) and 14.32 μ(M): 3H out-of-plane deformation vibration 8.67 μ (W): 1,2,3-substitution of benzene ring Probable structure: 1,2,3-trialkylbenzene

TABLE VI

ANALYSIS OF SYNTHETIC BLENDS

Blend	Component	Relative retention	Wt. % present	Wt. % found Run 1	Run 2	Run 3
A	Isopropylbenzene	0.82	10.28	10.31	10.47	10.77
	n-Propylbenzene	1.00	11.67	—	—	—
	1,3,5-Trimethylbenzene	1.29	12.93	12.91	12.82	12.61
	1-Methyl-2-isopropylbenzene	1.56	12.62	12.14	12.16	12.54
	Indan	1.82	19.07	18.08	18.60	18.34
	Indene	1.92	14.71	15.03	15.05	14.67
	1,2,3,5-Tetramethylbenzene	2.88	18.72	19.16	19.19	18.66
	Total		100.00	99.30	99.96	99.26
B	n-Propylbenzene	1.00	14.64	—	—	—
	sec-Butylbenzene	1.35	18.14	17.62	17.42	—
	1-Methyl-4-isopropylbenzene	1.48	15.23	14.91	14.97	—
	1-Methyl-3-n-propylbenzene	1.72	17.07	16.97	17.09	—
	1,3-Dimethyl-5-ethylbenzene	1.84	21.37	21.28	21.54	—
	1-Methylindene	2.23	13.64	13.54	13.76	—
	Total		100.00	98.96	99.42	—

For analyzing the components in the sample, a certain amount of the internal standard, n-propylbenzene, roughly 15% by weight, was added to each of the sample fractions so that the peak area of the standard was approximately equal to that of the major peaks. A new chromatogram of each fraction, after the addition of the standard, was then made. The percentage of each component was then calculated by using equation (1). In the few instances of unresolved components, conventional quantitative infrared analysis was used.

The aromatic hydrocarbons found in the low-temperature bituminous coal tar and their quantities are presented in Table VII. The values of wt. % in neutral oil for the highest boiling components are not entered, since it is expected that more of these compounds will be found in distillate fractions 7 and 8.

DISCUSSION

Correlation between relative retention and boiling points of alkylbenzenes having an equal number of carbon atoms

Desty and Whyman[12] plotted the boiling points of a large number of low-boiling paraffinic hydrocarbons and a few aromatic hydrocarbons against the logarithm of their relative retention volumes for two different stationary phases, resulting in two almost straight lines for each of the solvents. These plots indicate the selectivity of the two stationary phases for these two different types of solutes and offer help in choosing a suitable solvent for the separation of these two general types. However, no relationship between the relative retentions and boiling points of alkylbenzenes having an equal number of carbon atoms in the alkyl group has ever been expressed for the purpose of identifying this type of hydrocarbon. When the logarithms of relative retention for alkylbenzenes with an equal number of carbon atoms in the alkyl group were plotted against their boiling points, a straight line resulted. Fig. 2 shows five such lines corresponding to alkylbenzenes having 2, 3, 4, 5, and 6 carbon atoms in the alkyl groups. It is interesting to see that these lines are parallel to each other. There is a similar correlation at 200°C.

TABLE VII

ANALYSIS OF INDIVIDUAL AROMATIC HYDROCARBONS BOILING UP TO 200°C. IN NEUTRAL OIL DISTILLATE FRACTIONS

Compounds identified	Fractions	Method of identification	Source of I.R. spectrum	Total wt., g.	Wt. % in neutral oil[a]
Methylbenzene[b]	1,2	Rel. retention	—	1[c]	Trace
Ethylbenzene[b]	1,2	Rel. retention	—	2[c]	Trace
1,3- and 1,4-Dimethylbenzene[b]	1,2	Rel. retention	—	9[c]	Trace
1,2-Dimethylbenzene[b]	1,2	Rel. retention	—	20[c]	Trace
Isopropylbenzene[b]	1,2	Rel. retention	—	79[c]	Trace
n-Propylbenzene[b]	1,2	Rel.retention,I.R.	d	250[c]	0.002
1-Methyl-3-ethylbenzene[b]	1,2	Rel.retention,I.R.	e	0.010	0.001
1-Methyl-4-ethylbenzene[b]	1,2	Rel.retention,I.R.	e	0.0098	0.001
1-Methyl-2-ethylbenzene[b]	1,2	Rel.retention,I.R.	e	0.0075	0.001
1,2,3-Trimethylbenzene[b]	1,2	Rel.retention,I.R.	e	0.3105	0.045
1,2,4-Trimethylbenzene[b]	1,2,3	Rel.retention,I.R.	e	0.2695	0.039
1,3,5-Trimethylbenzene[b]	1,2,3	Rel.retention,I.R.	e	0.1184	0.017
1-Methyl-4-isopropylbenzene	1,2,3,4	Rel.retention,I.R.	d	0.0596	0.009
1-Methyl-3-isopropylbenzene	1,2,3,4	Rel.retention,I.R.	d	0.0511	0.007
1-Methyl-2-isopropylbenzene	3	Rel.retention,I.R.	d	0.0164	0.002
1,2-Diethylbenzene	3,4	Rel.retention,I.R.	e	0.0857	0.012
1,3-Diethylbenzene	3,4	Rel.retention,I.R.	e	0.1009	0.015
1,4-Diethylbenzene[b]	4	Rel. retention	—	0.0062	0.001
1,2-Dimethyl-4-ethylbenzene[b]	3,4,5,6	Rel. retention-b.p. correlation, I.R.	e	1.8139	0.260
1,4-Dimethyl-2-ethylbenzene	3,4,5,6	Rel. retention-b.p. correlation, I.R.	e	0.7698	0.110

(Table VII Continued)

Compounds identified	Fractions	Method of identification	Source of I.R. spectrum	Total wt., g.	Wt. % in neutral oil[a]
1,3-Dimethyl-5-ethylbenzene[b]	3,4,5,6	Rel.retention,I.R.	d	1.0872	0.156
1,2-Dimethyl-3-ethylbenzene[b]	4,5,6	Rel. retention-b.p. correlation, I.R.	e	0.5938	0.085
1-Methyl-3-n-propylbenzene	3,4,5	Rel.retention,I.R.	d	0.3180	0.046
1-Methyl-2-n-propylbenzene	5	Rel.retention,I.R.	d	0.0753	0.011
1,2,4,5-Tetramethylbenzene[b]	4,5,6	Rel.retention,I.R.	d	1.1066	0.159
1,2,3,5-Tetramethylbenzene	5,6	Rel.retention,I.R.	d	1.7690	0.253
1,2,3,4-Tetramethylbenzene[b]	6	Rel. retention-b.p. correlation, I.R.	e	0.8852	—
Indene[b]	1,2,3,4	Rel.retention,I.R.	e	0.2331	0.033
3-Methylindene	5,6	I.R.	e	0.5378	—
Indan[b]	1,2,3	Rel.retention,I.R.	d	0.3945	0.057
1-Methylindan	3,4,5,6	Rel. retention-b.p. correlation, I.R.	f	1.1265	0.161
5-Methylindan	5,6	Rel. retention-b.p. correlation, I.R.	f	1.4976	—
4-Methylindan[b]	5,6	Rel. retention-b.p. correlation, I.R.	f	1.4988	—
1,3-Dimethyl-2-n-propylbenzene	5	Rel. retention-b.p. correlation	—	0.0173	0.003
1,2-Dimethyl-3-n-propylbenzene	5,6	Rel. retention-b.p. correlation, I.R.-structural correlation	—	0.1008	—
1,4-Dimethyl-2-n-propylbenzene	5,6	Rel. retention-b.p. correlation, I.R.-structural correlation	—	0.4124	—

(Table VII Continued)

Compounds identified	Fractions	Method of identification	Source of I.R. spectrum	Total wt., g.	Wt. % in neutral oil[a]
1,4-Dimethyl-2-isopropylbenzene[b]	5	Rel. retention-b.p. correlation	—	0.1151	0.017
1-Methyl-3,5-diethylbenzene	5,6	Rel.retention,I.R.	d	0.2393	0.034
1-Methyl-2,4-diethylbenzene	6	Rel. retention-b.p. correlation, I.R.-structural correlation	—	0.6505	—
Styrene	1,2	I.R.	g	0.0332	0.005
4-Methylstyrene	1,2	I.R.	h	0.0225	0.003
β-Methylstyrene (trans)	1,2	Rel.retention,I.R.	d	0.1396	0.020
3-Phenyl-1-butene	1,2	I.R.	g	0.1163	0.017
1,2,3,4-Tetrahydronaphthalene	5,6	Rel.retention,I.R.	d	0.3171	—
Naphthalene[b]	6	I.R.	d	0.0886	—
Benzofuran[b]	1,2	Rel.retention,I.R.	d	0.0991	0.014
5-Methylbenzofuran 6-Methylbenzofuran	3 3,4	I.R. I.R.	g g	0.1432	0.021
2-Methylbenzofuran 3-Methylbenzofuran	4 4	I.R. I.R.	g g	0.1681	0.024
7-Methylbenzofuran	3,4	I.R.	g	0.0785	0.011

a Total neutral oil distilling up to about 360°C., representing 16.92 wt. % of the total tar.

b Previously identified by others[1,2,3,4,5].

c Ratio to methylbenzene.

d This laboratory.

e American Petroleum Institute, Research Project 44, infrared spectral data, Carnegie Institute of Technology, Pittsburgh, Pa.

f Jacob Entel, Clarence H. Rouf, and H. C. Howard, Anal. Chem. 25 (1953) 1303.

g Samuel P. Sadtler & Son, Inc., Philadelphia, Pa.

h Courtesy of W. F. Hamner, Monsanto Chemical Co., Texas City, Texas.

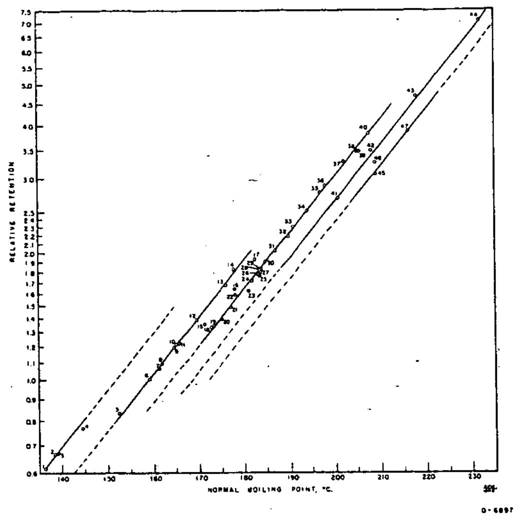

Fig. 2. Correlation between relative retentions and boiling points of some aromatic hydrocarbons at 150°C. on Apiezon L grease.

Legend:

1 Ethylbenzene
2 1,4-Dimethylbenzene
3 1,3-Dimethylbenzene
4 1,2-Dimethylbenzene
5 Isopropylbenzene
6 n-Propylbenzene
7 1-Methyl-3-ethylbenzene
8 1-Methyl-4-ethylbenzene
9 1,3,5-Trimethylbenzene
10 1-Methyl-2-ethylbenzene
11 α-Methylstyrene
12 1,2,4-Trimethylbenzene
13 1,2,3-Trimethylbenzene
14 Indan
15 Benzofuran
16 β-Methylstyrene
17 Indene
18 Isobutylbenzene
19 sec-Butylbenzene
20 1-Methyl-3-isopropylbenzene
21 1-Methyl-4-isopropylbenzene
22 1-Methyl-2-isopropylbenzene
23 1,3-Diethylbenzene
24 1-Methyl-3-n-propylbenzene
25 1-Methyl-4-n-propylbenzene
26 n-Butylbenzene
27 1,4-Diethylbenzene
28 1,2-Diethylbenzene
29 1,3-Dimethyl-5-ethylbenzene
30 1-Methyl-2-n-propylbenzene
31 1,4-Dimethyl-2-ethylbenzene
32 1,2-Dimethyl-4-ethylbenzene
33 1-Methylindan
34 1,2-Dimethyl-3-ethylbenzene
35 1,2,4,5-Tetramethylbenzene
36 1,2,3,5-Tetramethylbenzene
37 5-Methylindan
38 4-Methylindan
39 1,2,3,4-Tetramethylbenzene
40 1,2,3,4-Tetrahydronaphthalene
41 1,3-Diethyl-5-methylbenzene
42 2-Methylindene
43 Naphthalene
44 Pentamethylbenzene
45 1,2-Diisopropylbenzene
46 1,4-Diisopropylbenzene
47 1,3,5-Triethylbenzene

Indans and tetralin, which have a benzene nucleus and a fused saturated ring, fall closely on the correlation curves for alkylbenzenes with the corresponding number of carbon atoms in the alkyl group and, therefore, are included in these series. Indenes, styrenes, and naphthalene which have a double bond in the "side chain," however, do not follow the corresponding curves and appear to have a different pattern. From the limited data obtained at present, no correlation can be found for these types.

These correlation curves can be expressed by the following empirical equation:

$$\text{Log } V_R = mT_B - c \tag{2}$$

where V_R = relative retention of an alkyl benzene,

T_B = normal boiling point of the compound, °C.,

m = slope,

c = Y - intercept at any temperature; 0°C. arbitrarily selected.

The slope for the set of five alkylbenzene series at 150°C. on a stationary phase of Apiezon L grease is 0.0135, and their intercepts on the vertical axis at 0°C. are 2.0496, 2.1442, 2.2154, 2.2760, and 2.3215 for alkylbenzenes with 2, 3, 4, 5, and 6 carbon atoms in the alkyl group. The values of the intercept c are, of course, a measure of the separation of the five parallel lines from each other.

The intercept c in eq. 2 can be correlated with the number of carbon atoms in the alkyl group, N_C, as shown in Fig. 3. This can be expressed as follows:

$$\text{Log } N_C = a \log c - b \tag{3}$$

where N_C = number of carbon atoms in the alkyl group,

a = slope,

b = intercept.

For the curve shown in Fig. 3, a = 8.78 and b = 2.431.

From eq. 3, it is possible to generate a family of relative retention-boiling point curves when only one is known.

The relationship between relative retentions and boiling points of alkylbenzenes was found to be very useful for characterization. For example, peak 6 in the chromatogram shown in Fig. 1 has a relative retention of 2.16. By checking the curves in Fig. 2, it was readily determined that the boiling point of this unknown in a distillate fraction boiling at about 192-198°C. should be 189.3°C. if it is an alkylbenzene having four carbons in the alkyl group or 193.8°C. if it has an alkyl group of five carbon atoms. 1,2-Dimethyl-4-ethylbenzene boils at 189.79°C. and 1-methyl-3-isobutyl- and 1-methyl-3-sec-butylbenzene both boil at 194°C. The infrared spectrum of the collected material producing this peak agreed very well with that of 1,2-dimethyl-4-ethylbenzene.

<u>Calibration factor (f_C) and type of aromatic hydrocarbon</u>

An examination of the calibration factor, f_C, data in Table III disclosed that the molecular structure of the compounds plays an important role in determining the value of this factor, while within each type the variation in value is relatively small. Referring to Table III, for all alkylbenzenes the values are from

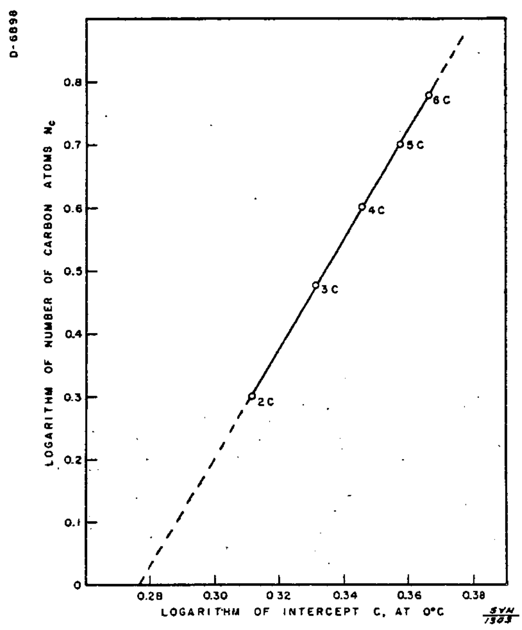

Fig. 3. Correlation between number of carbon atoms in the alkyl group, N_C, and intercept C at 0°C.

0.93-1.10 with an average of nearly 1.0; for indenes, styrenes, and naphthalene, 1.15, 1.1, and 1.14; and for indan and tetralin, 1.65 and 2.05. Considering the benzene nucleus as a common structural center for all compounds, the alkylbenzenes are obviously in one group; styrenes, indenes, and naphthalene, which all have unsaturation in the other part of the molecule, form another group; indan and tetralin, with the non-benzene part being saturated and cyclic, are different from the other two groups. The difference between indan and tetralin is probably due to the number of carbon atoms in the saturated cyclic part of the molecule. It is interesting to note that benzofuran, having an unsaturated part in addition to the benzene nucleus, has a value of 1.15, quite similar to that of the second group although it contains an oxygen atom.

Based on this observation about the f_C values and structures, f_C values for some hydrocarbons which were not available in this laboratory were assumed to be equal to those of either their isomers or of structurally similar compounds. Thus, f_C, 1.09, for 1,3-dimethyl-5-ethylbenzene was used for estimation of all dimethylethyl benzenes; 1.11 for 1-methyl-3,5-diethylbenzene for all methyldiethyl benzenes; 1.65 of indan for all methyl indans; 1.15 of benzofuran for all methyl benzofurans, and 1.00, an average value for 1,2,4,5- and 1,2,3,5-tetramethylbenzene, for 1,2,3,4-tetramethylbenzene.

ACKNOWLEDGEMENTS

The authors wish to thank Joseph R. Comberiati for his help in distillations and Theodore L. Yarboro for his synthesis of the two methylindenes used in this work.

REFERENCES

1 A. JÄGER and G. KATTWINKEL, Brennstoff-Chem., 35 (1954) 353.
2 G. T. MORGAN and A. E. J. PETTET, J. Soc. Dyers Colourists, 54 (1938) 17.
3 A. PARANT, Compt. rend. congr. ind. gaz. Paris, 65 (1948) 409.
4 R. WEISSGERBER, Brennstoff-Chem., 5 (1924) 208.
5 D. H. DESTY, Ed., Vapour Phase Chromatography, Academic Press, Inc., New York, 1957, p. 419.
6 C. H. FISHER and A. EISNER, Ind. Eng. Chem., Anal. Ed., 9 (1937) 213.
7 R. M. GOODING and R. L. HOPKINS, The Determination of Aromatics in Petroleum Distillates; presented at the Chicago meeting of the Am. Chem. Soc., September 9-13, 1946.
8 G. U. DINNEEN, C. W. BAILEY, J. R. SMITH and JOHN S. BALL, Ind. Eng. Chem., Anal. Ed., 19 (1947) 992.
9 D. H. DESTY, Ed., Vapour Phase Chromatography, Academic Press, Inc., New York, 1957, p. xiii.
10 L. T. BELLAMY, The Infrared Spectra of Complex Molecules, John Wiley & Sons, Inc., New York, 1956, p. 54.
11 A. I. M. KEULEMANS, A. KWANTES, and G. W. A. RIJNDERS, Anal. Chim. Acta, 16 (1957) 29.
12 D. H. DESTY and B. H. F. WHYMAN, Anal. Chem., 29 (1957) 320.